Letters to the Editor

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23

THE CRYSTAL STRUCTURE OF α-LEAD AZIDE, α-$Pb(N_3)_2$

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α-Lead Azide crystallizes in the Orthorhombic system, Space Group $Pna2_1$; $Z = 12$; calculated density $= 4.705$; $a = 6.65$ Å, $b = 11.37$ Å, $c = 16.32$ Å. Earlier studies of this crystal were made by Miles (1931), Pfefferkorn (1948) and Azároff (1956). Azároff came to the conclusion that the Space Group is either Pcmn or $Pc2_1n$, and that no distinction can be made between these two Space Groups on the basis of the lead positions. Asymmetric nature of the azide group led Azároff to believe that the Space Group is $Pc2_1n$. Subsequent three-dimensiona refinement carried out by the author of the lead positions given by Azároff showed that the *R*-factor comes down considerably if the noncentrosymmetric Space Group is assumed. $Pna2_1$ was adopted instead of $Pc2_1n$ in order to conform to the IBM 704 programming.

Three dimensional X-ray data using $Cu_{K\alpha}$ radiation were collected by the author at the Crystal Research Laboratory, The Pennsylvania State University. This compound has the properties of a detonator, and considerable experimental difficulties were encountered while taking the three-dimensional X-ray data. $Mo_{K\alpha}$ radiation could not be used since it was found that the crystals, when irradiated, started to disintegrate after three or four days. Linear absorption coefficient for $Cu_{K\alpha}$ radiation was found to be extremely high ($\mu = 819$ cm.$^{-1}$), and hence it was necessary to correct for absorption. The crystals could not be made into cylinders because of the danger of explosion. A uniform cylindrical absorption correction for the crystals was assumed, though the crystals were prismatic and somewhat rhombic in cross-section. After 3 to 4 days' irradiation, the crystals started to disintegrate, and hence separate crystals had to be used to obtain data for each layer. Data on six layers (971 observable reflections) were collected in

this fashion. Since "*a*" was the zone axis for the prisms and the crystals could not be cut across the prism faces without the danger of explosion, it was not possible to obtain *hk0* or *h01* data. The three-dimensional data were scaled and rescaled after each phase of IBM computation by calculating scale factors ($\Sigma F_o/\Sigma F_c$) for each layer from structure factor calculations. Owing to these experimental difficulties it was assumed that the X-ray data would not be too accurate, though they were subsequently found to be accurate enough for distorted nitrogen peaks to appear in the three-dimensional Fourier sections calculated with lead positions only. More reliance was placed on the *0kl* neutron data for absolute confirmation of the the structure determination, collected by Danner and Kay at the Brookhaven National Laboratory.

Structure Determination

Consideration of two sets of strong reflections (006 and 203 for Space Group Pnma) led Azároff (1956) to propose the following approximate coordinates of the lead atoms :

8 Pb atoms in (*d*)	$x = \sim 3/8$	$y = 0.130$	$z = 0.083$
4 Pb atoms in (*c*)	$x = \sim 1/8$	$y = 0.870$	$z = 1/4$

Structure factors calculated with these coordinates were used by the author to scale different layers. These coordinates were then used for three-dimensional refinement of the lead positions using Space Group $Pna2_1$. The *R*-factor dropped from 0.62 to 0.45. The observed data for different layers were then rescaled and further refinement of the lead positions resulted in the following coordinates :

4 Pb atoms in (*a*)	$x = 0.331$	$y = 0.136$	$z = 0.084$
4 Pb atoms in (*a*)	$x = 0.344$	$y = 0.122$	$z = 0.407$
4 Pb atoms in (*a*)	$x = 0.069$	$y = 0.872$	$z = 0.237$

The *R*-factor dropped from 0.42 to 0.36.

At this stage the three-dimensional Fourier sections began to show distorted peaks in the non-lead positions, and approximate coordinates for nine nitrogen atoms could be found out. The coordinates of these nine atoms were then used in conjunction with the refined lead positions for the next cycle of refinement. The *R*-factor dropped from 0.32 to 0.21. Positions of the rest of the nitrogen atoms could be discerned in the new three-dimensional Fourier sections, though considerable difficulties were encountered because of the presence of ripples around the lead peaks, which sometimes rather obscured the nitrogen peaks.

Approximate coordinates of the lead and nitrogen atoms in the structure of α-lead azide has thus been ascertained with the help of three-dimensional X-ray data, and they are listed in Table I :

TABLE I

Type of atom				
Pb	0.064	0.867	0.240	3.532
Pb	0.344	0.119	0.406	3.252
Pb	0.333	0.131	0.084	3.835
N	0.163	0.281	0.184	2.50 approx.
N	0.154	0.276	0.251	2.50 ,,
N	0.146	0.271	0.326	2.50 ,,
N	0.098	0.228	0.488	2.50 ,,
N	0.108	0.267	0.560	2.50 ,,
N	0.116	0.300	0.624	2.50 ,,
N	0.122	0.284	0.860	2.50 ,,
N	0.110	0.262	0.924	2.50 ,,
N	0.100	0.239	0.996	2.50 ,,
N	0.500	0.490	0.365	2.50 ,,
N	0.362	0.498	0.407	2 50 ,,
N	0.213	0.506	0.443	2.50 ,,
N	0 875	0.468	0.243	2 50 ,,
N	0.025	0.528	0.240	2.50 ,,
N	0.163	0.592	0.237	2.50 ,,
N	0.475	0.495	0.117	2.50 ,,
N	0.337	0.489	0.084	2.50 ,,
N	0.188	0.481	0.048	2.50 ,,

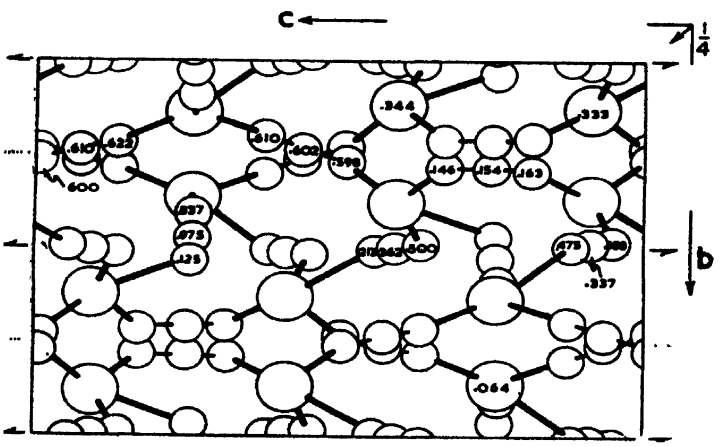

Fig. 1. Approximate Structure of α-Pb $(N_3)_2$
O—lead O—nitrogen

A diagrammatic representation of the structure in the 0*kl* plane has been shown in Fig. 1.

The observed data require about two or more cycles of refinement and data for each layer require rescaling after each cycle of refinement.

0*kl* structure factor calculations were made with the S-FAC giving equal weight to the lead and nitrogen atoms (neutron scattering length for lead is 0.96×10^{-12} cm. and that for nitrogen is 0.94×10^{-12} cm.) and using the coordinates listed above. The calculated data has been compared to the observed 0*kl* neutron data for α-$Pb(N_3)_2$, and the correspondence between the observed and calculated structure factors for low and moderately high order reflections was found to be quite good. It may be difficult to refine the neutron data owing to the overlap of several nitrogen and lead atoms in the 0*kl* projection, as shown in Fig. 1.

DISCUSSION OF THE STRUCTURE

A 4-fold configuration of nitrogen atoms around lead (Fig. 1), somewhat intermediate between a distorted pyramid and a square, can be postulated in the case of α-lead azide.

From bond energy considerations Pauling and Brockway (1937) have shown that the linear azido group will be asymmetric if the bonding is homopolar, as in the case of α-lead azide. Indications of this are already evident in the case of α-lead azide, and further refinement of the structure will most probably confirm this. In most organic and metal azides it has been found that the angle between the nitrogen atoms at the ends of the azide group and the heavy atom or molecular group attached to them is apparently 120° (Wells, 1945) and this has also been found to be true in the case of α-lead azide.

Further refinement of the structure is required to calculate accurate bond distances and bond lengths.

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